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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds” *by* M. E. Jenkin et al.

M. E. Jenkin et al.

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We are grateful to both referees for their generally very supportive comments on the paper, and concerning the Master Chemical Mechanism itself. Neither referee has any substantial criticisms of the paper, but each raises a number of comments and queries which have either been reflected in minor amendments to the paper, or are replied to below.

Referee 1, comment 1: Secondary organic aerosol formation

The referee notes the omission of a substantial discussion of the formation of secondary organic aerosol (SOA) from aromatic oxidation. The main aim of the paper is

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to describe the methodology used to construct gas phase degradation mechanisms for aromatic VOC, and the formation of SOA is deliberately not discussed in detail. As indicated in the conclusions section, the MCM v3 schemes provide a good starting point for the inclusion of a detailed chemical representation of gas aerosol product partitioning, and this is a major focus of ongoing work, albeit at a very preliminary stage. In conjunction with observations of SOA formation in chamber systems, early indications from the mechanistic work are that significant formation of SOA is not initiated until second- or subsequent generation products are formed. However, once organic aerosol is present in substantial amounts it is likely that (probably small) proportions of even some of the lower volatility first generation products can be present in the condensed phase.

Referee 1, comment 2: Degradation of VOCs to CO2 and water

With reference to the statement "This process is continued until the chemistry either yields CO2, or until an organic product or radical is generated for which the subsequent chemistry is represented elsewhere in MCM v3" (page 1908, lines 15-17), the referee points out that the complete gas phase degradation of aromatic VOCs to CO2 and water in the atmosphere may be intercepted by gas-aerosol transfer of some intermediate products. As indicated above, the authors are in complete agreement with this opinion. However, the present paper and, in particular the section where this statement appears, is describing the methodology used to construct gas phase degradation mechanisms for aromatic VOC. We therefore feel that the discussion of aerosol formation processes at this point would impair the clarity and purpose of the section. To emphasise that gas phase chemistry alone is being discussed, the first sentence of the section has been altered to read "The protocol, outlined in section 4, is designed to allow the construction of comprehensive, consistent gas phase degradation schemes for aromatic VOC in MCM v3".

Referee 1, comments 3 - 6: Reported product studies

The referee provides an informative summary of a series of publications which are relevant to the present paper. Some of these have been published since the beginning of 2001 (when construction of MCM v3 commenced), but the results have been considered in related subsequent work (e.g. as described by Wagner et al., 2002), and will contribute to future aromatic mechanism development work. Many other studies identified by the referee have helped define the present protocol. However, reference to the highly relevant paper of Bethel et al. (2000) was overlooked when the paper was written, although the results of that study were taken into consideration. The paper of Bethel et al. (2000) is thus given due recognition at a number of points in the revised manuscript. The authors are very grateful to the referee for these contributions to the discussion.

Referee 1, comment 7: Formation of 1,6-dicarbonyl-2,4-dienes

The referee notes that no mention is made of the potential formation of 1,6-dicarbonyl-2,4-diene products in aromatic systems. The authors are aware that evidence for the formation of these compounds has been reported (e.g. Kwok et al., 1997), and recognise that they are almost certainly formed under certain experimental conditions. However, the accepted mechanism for the formation of these products relies on efficient conversion of the 1,2-hydroxycyclohexadienyl type RO2 radicals to the corresponding RO radicals (e.g. by reaction with NO). As discussed in section 4.5.3, the weight of evidence is consistent with these complex RO2 radicals undergoing rapid unimolecular rearrangements, which dominate under atmospheric conditions, and under conditions generally employed in more recent chamber studies (e.g., Wagner et al., 2002). Given that the MCM v3 schemes have been constructed on this basis, the authors feel that the specific discussion of products of reaction channels that have been excluded (with justification) would lessen the clarity of an already highly detailed paper. It should be noted that the study of Kwok et al. (1997) is fully cited.

Referee 2: Canonical forms of the hydroxycyclohexadienyl radical

The referee correctly points out that the canonical forms used to represent a resonance-stabilised radical do not actually exist independently. The authors acknowledge that the sentence in question (page 1910, line 23) was poorly worded, and this has been modified to read "Furthermore, each resultant OH-aromatic adduct (i.e. a hydroxycyclohexadienyl radical, with alkyl substitutions where appropriate) is resonance-stabilised, such that subsequent reaction (e.g. with O2) can potentially take place at up to three positions."

Referee 2: Classification of substituent alkyl groups

With reference to the phrase "For aromatics containing alkyl groups which are not identical, e.g., 1,2,4-trimethylbenzene..." (page 1914, line 13), the referee queries the stated non-equivalence of the alkyl groups in 1,2,4-trimethylbenzene. The criterion applied for alkyl groups to be identical, is that they must have the same structural formula (i.e. CH3-, C2H5- etc.) and be located in the same chemical environment. The methyl groups in 1,2,4-trimethylbenzene are not identical, by virtue of each being in a different environment. This is clear in the context of the discussion, which reflects that the abstraction of H in each case leads initially to a different radical and, subsequently, to a different aldehyde product.

Referee 2: Reactions of RO2 radicals from 1,4 addition of OH and O2

The referee points out that no explanation is given for treating the 1,4-hydroxycyclohexadienyl peroxy radicals as conventional RO2 radicals. They are treated in this way because they are essentially allyl peroxy radicals in character, and studies of such RO2 radicals (e.g., Jenkin et al., 1993; 1998) have confirmed that their reactions are broadly similar to those of simple alkyl peroxy radicals. Accordingly, the text of section 4.5.2 has been expanded to clarify this point.

References

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